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BTX and carbonyl compounds in the roadside environment of Inezgane-Ait Melloul (southwestern Morocco)

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Abstract

The concentrations of carbonyl compounds (formaldehyde, acetaldehyde, benzaldehyde and acetone) and BTX compounds (benzene, toluene and o-m-p-xylenes) were measured in 2012-2014 at eight roadside locations of the Inezgane-Ait Melloul urban community, in southwestern Morocco. We used active sampling onto SKC activated charcoal tubes for BTX, followed by GC-FID detection, and onto DNPH cartridges for carbonyls, followed by HPLC/UV analysis. The most abundant carbonyl compound is acetone (20.0 ± 4.7 $\mu g.m^{-3}$), then formaldehyde (18.9 ± 5 $\mu g.m^{-3}$), acetaldehyde (17.8 ± 4.3 $\mu g.m^{-3}$) and benzaldehyde (4.3 ± 1.3 $\mu g.m^{-3}$). Toluene was the most abundant aromatic compound (10.8 ± 1.6 $\mu g.m^{-3}$), followed by xylenes (10.1 ± 2.9 $\mu g.m^{-3}$) and benzene (4.8 ± 1.2 $\mu g.m^{-3}$). These values, in the range of previous studies of the ambiant air in cities over the world, confirm that the pollution pattern in the Inezgane Ait Melloul area is mainly influenced by the local traffic, and not by remote background sources. Based on the concentration ratio of formaldehyde and toluene, the relative proportion of formaldehyde produced by photochemical reactions has been evaluated to 20% in winter, and 40% in summer.

1. Introduction

Over the last two decades, the Moroccan economy has undergone a very fast growth, with a rapid urbanization and industrialization. The industrial units are often located within the cities or close to them. There has also been a significant increase of the number of private vehicles to respond to the transportation demand, because of the shortcomings or lack of public transportation. The capacity of the road system is greatly exceeded and slow traffic is often observed, especially at rush hours, affecting the overall quality of life of urban residents. The Moroccan fleet, running mainly (75%) on diesel fuel [1], is composed of over 3.4 million in 2014. It includes ~2.400.000 private vehicles, ~1.000.000 trucks and buses, and ~40.000 motorcycles [2]. The fleet is still relatively old, with 63% of private vehicles being over 5 years, and 55% of trucks over 10 years, with 22% over 20 years [1].

This situation elicits numerous environmental and health concerns, including air quality. Specific actions have been taken to protect air quality, such as setting incentives for increasing the renewal rate of the car fleet, turning to vehicles with catalytic converters, and promoting the use of cleaner fuels. In this context, the public authorities have decided that the characteristic of vehicle fuels (gasoline and diesel) should be the same as the European ones by 2008. The unleaded gasoline and low sulfur diesel fuel, containing until now 0.005% of sulfur, will be replaced by 0.001% sulfur in November 2016. In addition, a strict enforcement of the law aiming at the protection of the environment has been set up, and a national network for the monitoring of atmospheric pollutants was installed. This network monitors NOx, O_3, CO and SO_2, but not the levels of VOC such as carbonyl compounds or BTEX (benzene, toluene, ethylbenzene and xylenes).

Carbonyl compounds and BTEX have recognized adverse effects on health [3, 4, 5]. They also play a key role in the atmospheric (photo)chemistry [6], where for instance their reaction with NOx under sunlight leads to the formation of ozone and secondary organic aerosols (SOA) [7, 8, 9]. The photodegradation of aldehydes produces hydroxyl (OH) and peroxy (HO_2, RO_2) radicals, increasing the oxidizing properties of the atmosphere [10, 11, 12, 13].

Benzene (C_6H_6) is classified as a Class 1 carcinogen [14]. Toluene (C_7H_8) is the most abundant in air [15], and xylenes (C_8H_{10}) are regarded as the most reactive compounds in the BTEX family. Formaldehyde, omnipresent in both indoor and outdoor air, is also carcinogenic and linked to respiratory diseases [4-14, 16, 17].

The BTEX species come only from the primary sources of human activities, while the carbonyl compounds are both primary pollutants directly emitted by the fixed and mobile pollution sources [18], as well as secondary pollutants formed by (photo)-chemical reactions involving primary pollutants [9-17, 19]. BTEX and carbonyls are commonly related to vehicle emissions [6, 20, 21], especially in metropolitan cities [19, 22, 23]. The concentrations of BTEX and carbonyls in urban air are therefore the object of many studies over the world [9-24], especially in developing countries where standards for the emissions or ambient concentrations have generally not been established.

There is to our knowledge no report about the BTEX and carbonyls levels in the ambient air of the Moroccan largest cities, except our previous work on pollutants quantification and source identification in the Agadir area in the southwestern part of Morocco [25, 26, 27], and the study by Zouir et al. [28] of the Tangiers zone (north of Morocco). The present study investigates the BTX and carbonyl compounds (formaldehyde, acetaldehyde, acetone, and benzaldehyde) in the roadside environment of the Inezgane-Ait Melloul area (Agadir region).

2. Materials and methods

2.1. General description of the study zone

The urban community of Inezgane-Ait Melloul (Figure 1), with more than 541.000 inhabitants [29] distributed over 293 km^2, is located in southwestern of Morocco, about 15 kilometers from Agadir city (30°21'N, 9°31'W).

The climate is semi-arid to arid, influenced by several factors: the Atlas mountain region, the Atlantic Ocean coast and the desert. The aridity increases from west to east. The average annual rainfall is about 260 mm. The annual average maximum and minimum temperatures are 27°C (August) and 11°C (January) respectively, with a relative humidity ranging between 32 % and 85 %. The wind is mostly in the west-northwest direction, with wind speed varying 0.1 to 3.3 m/s. As already stressed in our previous paper [25], these specific meteorological conditions can create a temperature inversion leading to an accumulation of the pollutants in the lower layer of the atmosphere.

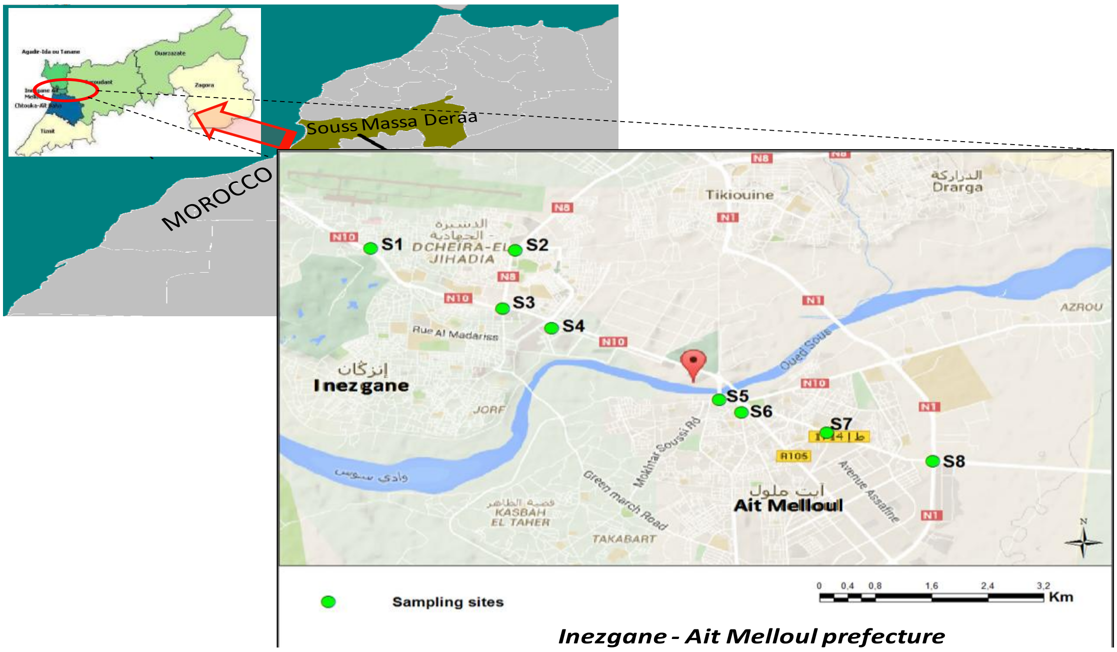

Figure 1: Map of Morocco and of the Inezgane-Ait Melloul area, indicating the position of the sampling sites (S1 to S8).

In addition to local small-size industries, the Inezgane-Ait Melloul area has two large industrial zones, Tassila and Ait Melloul, with over 125 production units. These units include food industries (production of fish meal and fish oil), chemical processes (production of plastics, adhesives, pesticides, fertilizers …), pharmacochemical units, metallic industries and leather industries. The Inezgane-Ait Melloul area is also a central hub of daily transit, with two national roads (NR1 and NR10), and the largest intercity bus station in southern Morocco.

2.2 Position and description of the sampling sites

We selected eight sites in the Inezgane Ait Melloul area, taking into account the proximity of traffic and of local industrial units. Sites S1 to S4 are located in Inezgane and S5 to S8 in Ait Melloul. The positions of the sampling sites are shown on Figure 1. Table 1 describes their characteristics and their immediate environments. In each location, the sample point was located at a height of 1.8 m above the ground. The carbonyl and BTX concentrations at these sites were measured as detailed below.

Table 1: Characteristics of the sampling sites

site	Area	Coordinates	Placement and description
1	Inezgane	30°22'18.2"N 9°33'02.1"W	Near a major crossroad, close to the forest area that extends along the road. Intense traffic coming from Agadir and Essaouira cities.
2		30°22'17.1"N 9°31'55.0"W	Site located at the entrance of the Dcheira town, on the road to Agadir. High traffic flow in the daytime. The sampling site is located a few meters away from wood industry and packaging company.
3		30°21'45.5"N 9°32'00.9"W	Near Central police station of Inezgane city, at a crossroad with heavy traffic coming from Agadir and Dcheira for transit to Ait Melloul. Surrounded by low rise buildings.
4		30°21'34.8"N 9°31'38.2"W	Located between the largest bus station and the commercial center. Many thousands of old Diesel cabs and private vehicles. This site is one of the most congested traffic area of the zone under study.
5	Ait Melloul	30°20'56.4"N 9°30'21.0"W	Site located at the entrance of the town. All road traffic passes through this point not far from the sewage pumping station (many odor-related complaints).
6		30°20'49.4"N 9°30'10.8"W	Located in the middle of three lanes of heavy traffic in both directions. This site is also downwind of industrial units.
7		30°20'38.4"N 9°29'31.2"W	Dense traffic road, not far from the industrial zone of Ait Melloul city.
8		30°20'23.0"N 9°28'42.2"W	At the crossroad of the national road NR1 and express road connecting Agadir to Al Massira International Airport. Heavy vehicle traffic. Windy zone

Measurements were performed between March 2012 and December 2014. Most of the time, the samples were collected during sunny weather, with peak solar irradiation occurring in the early afternoon (12:00-16:00, Morocco time). In summer, warm conditions dominated and daytime temperature ranged from 16°C to 37°C. In winter period, the temperature ranged from 11°C to 26°C.

2.3. Sampling and analysis of carbonyls

The measurement of carbonyls is based on the conventional derivatization technique [30], and is briefly desvribed here. More details can be found in our previous work [24-26]. Carbonyls were trapped by reaction with 2,4-dinitrophenylhydrazine (2,4-DNPH) in a cartridge filled with silica gel (60-130 mesh) prealably coated with an acidified 2,4-DNPH solution leading to the production of stable hydrazones. The cartridges consist of Pyrex tubes (12 cm length, 1.2 cm i.d.), wrapped in alluminium foil to shield them from direct sunlight. After preparation, the cartridges were dried in a vacuum desiccator during 2-3 days before being sealed and and stored in a refrigerator until their use**.** During sampling, the 2,4-DNPH cartridge was preceded by a second cartridge filled with potassium iodide (KI) acting as an ozone trap [9-31, 32,33]. Ambient air volumes ranging between 310 and 418 L were sampled at a flow rate of 2.5 to 3.5 $L.min^{-1}$ for a duration varying between 1 and 2 hours, using calibrated flowmeters and a battery-operated pump (KNF NPK).

After sampling, the cartridges were eluted with 20 mL of acetonitrile. The extracted derivative solutions were weighted and a 20 µL aliquot was analyzed by HPLC-UV, using a Flexar HPLC system (Perkin Elmer) with an isocratic pump. Separation was achieved with an Agela Technologies XBP C18 column (5 µm, 250×4.6 mm). Detection was performed with a UV-visible detector ajusted at 360 nm. Acetonitrile (HPLC grade)-water (60/40) was used for the mobile phase, flowing at 1.5 $ml.min^{-1}$, which allowed a correct separation of the hydrazones corresponding to the $HC(O)H$, $CH_3C(O)H$, $C_6H_5C(OH)$ and $(CH_3)_2CO$. Other hydrazones corresponding to the other carbonyls such as acrolein, propionaldehyde, hexanal, crotonaldehyde, butyraldehyde, valeraldehyde, were present in the chromatograms but their corresponding carbonyls were not quantified in this study.

The mass of hydrazones was determined using the HPLC peak areas. Calibration curves were obtained from standards prepared according to the method described by Levart and Veber [34]. They were linear for the concentration ranges used in this work, i.e. between 0.5 and 10 mg/L for each hydrazone, with a correlation coefficient of 0.97 or higher. The concentrations of aldehydes in the air were derived from the mass of hydrazones, the sampling time and the sampling flow:

$$[P] = \left(m\ /\ (Q \times t)\right) \times 10^6 \qquad (1)$$

Where m (g) is the mass of analyte P (in µg) quantified in the extracted solution, Q is the sampling rate (mL/min) and t is the sampling time (min). For each series of prepared DNPH cartridges, two were used to determine the blank values (background carbonyl concentrations) and the resulting analyses showed a low residual mass of ~ 0.45 µg and 0.8 µg for formaldehyde and acetaldehyde respectively. The aldehyde detection limits for a sampling time of 2 hr were 0.42 $\mu g.m^{-3}$ for formaldehyde, 0.59 $\mu g.\ m^{-3}$ for acetaldehyde, 0.73 $\mu g.m^{-3}$ for acetone and 0.98 $\mu g.m^{-3}$ for benzaldehyde.

The precision of the method was evaluated by running two sampling systems in parallel. Five pairs of samples were analyzed, leading to relative standard deviation (RSD) values of 13.29 % for HC(O)H, 15.17 % for $CH_3C(O)H$ and 11.94 % for $(CH_3)_2CO$. To determine the carbonyl recovery factors, three cartridges spiked with 2 µL of a mixture of 1 mg/mL solution of each carbonyl were analysed, which showed recovery factors in the ranges 90-109 %, 94-115 %, 89-100 % and 93-113 % respectively for formaldehyde, acetaldehyde, benzaldehyde and acetone. The breakthrough of carbonyls was also studied by sampling air through two cartridges connected in series. Less than 5 % of carbonyls was measured in the second cartridge, indicating only minor breakthrough.

2.4. Sampling and analysis of BTX

We followed the USA-EPA methodology [30] for the measurement of BTEX. They were sampled as in our previous work [27] by drawing air through charcoal tubes (70 mm long, 4 mm i.d., particle size 20/40 mesh, reference 226-01 from SKC Inc.) containing two beds (a 100-mg section and a 50-mg section) separated by urethane foam. The aromatic compounds were sampled during 60 to 120 min with a flow of 0.6 to 1 $L.min^{-1}$. As soon as the pump was turned off, the SKC sorbent tubes were disconnected from the sampling system, labeled, and the two extremities were tightly closed with special caps to avoid desorption and contamination. The samples were immediately placed into closed special plastic bags and kept at 4°C until analysis, within 2 to 8 days.

In order to detect breakthrough, two tests were performed: analysis of the second section of the SKC tube, which indicated that less than 12 % of the BTX compounds were trapped in this portion. The second test was based on a few experiments carried out with two SKC tubes connected in series. In this case, the results indicated no significant BTX levels (< 5 %) were collected in the second tube. For that reason, a single sorbent tube was used most of the times to sample BTX in ambient air.

Before analysis, the content of both sorbent sections of SKC tubes was transferred into 4 mL vials, weighed and extracted by adding 2 or 3 mL of cold dichloromethane CH_2Cl_2 (below 5°C to prevent losses by volatilization) with agitation during 20 or 30 min [33]. Carbon disulfide (CS_2) was not used here because of its high toxicity, even though it is the preferred solvent for charcoal tubes extraction. Analysis and quantification were performed by injection of 2 µL of the extracted solution in an Agilent 6890 gas chromatograph coupled to a FID detector. Samples were separated with a capillary column (Restek, Rtx®-5, Crossbond® 5 % diphenyl/95 % dimethyl polysiloxane, 30 m long, 0.32 mm internal diameter, 0.25 µm thickness). The carrier gas was helium, delivered at a flow rate of 1.5 $mL.min^{-1}$. The injection temperature was 300 °C in splitless condition with an injection volume of 1 or 2 µL. The oven temperature of the gas chromatograph was initially held at 60 °C for 4 min, then raised at a rate of 10 °C/min up to 180°C and finally kept constant at this temperature for 6 min [25]. Figure 2 shows an example of chromatogram of a sample of BTX.

The concentrations of the BTX compounds were derived from external calibration curves obtained with 0.5 or 13.5 $mg.L^{-1}$ of BTX prepared in refrigerated pure dichloromethane (benzene : Riedel de Haan, purity 99 % ; toluene : Prolabo, purity 99 % ; m,p,o-xylenes : Sigma-Aldrich, purity 98 % ; dichloromethane : Sigma-Aldrich, purity > 99.9 %) [27]. In order to control the quality of samples and analysis, the reproducibility of the data was checked by analysis of duplicate samples, for which usually differences of less than 12 % were observed. To determine the residual BTX concentrations, unexposed SKC tubes were analyzed before each analysis of samples in all measurement series. The amounts of some residues of benzene (~ 0.05 µg) and toluene (~ 0.02 µg) found in blanks never exceeded 12 % of any result in this work. No xylenes were detected in the blanks.

As for the carbonyl compounds, the concentrations of BTX in the air were derived from the mass of analyte, the sampling time and the sampling flow. The BTX detection limits for a sampling time of 1 h were estimated to be 0.31 $\mu g.m^{-3}$ for benzene, 0.26 $\mu g.m^{-3}$ for toluene and 0.37 $\mu g.\ m^{-3}$ for xylenes.

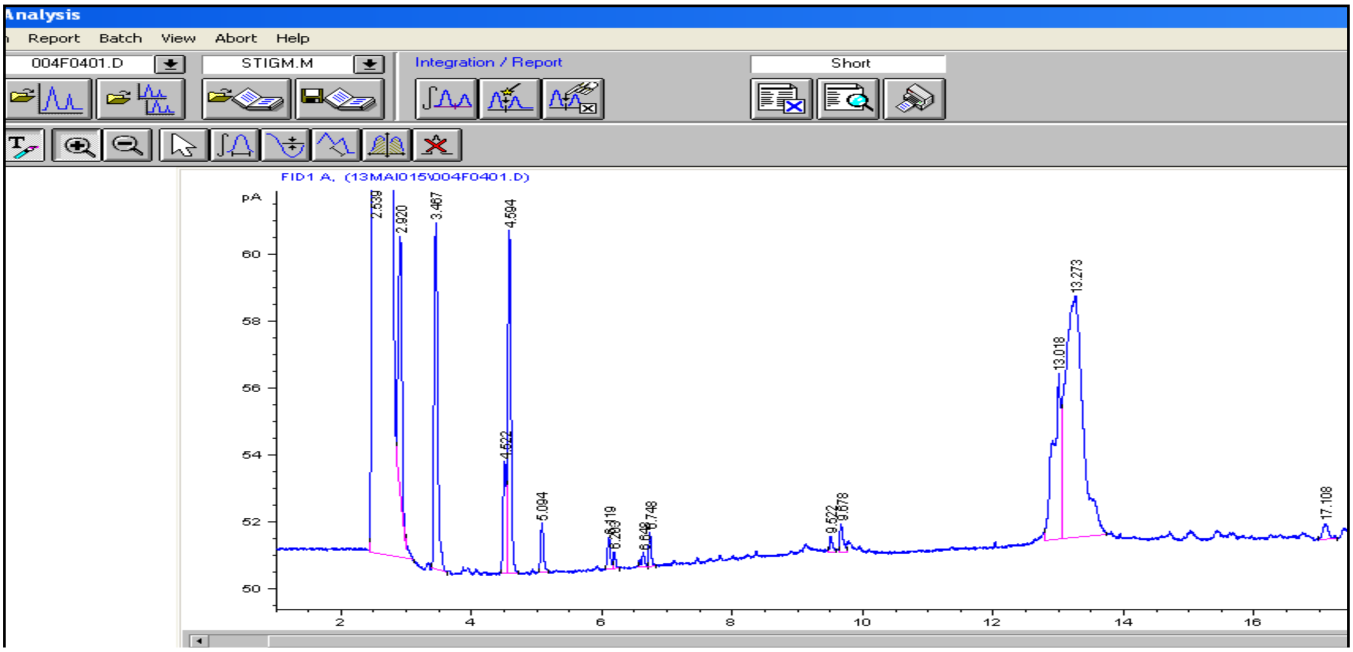

Figure 2: Example of chromatogram of a sample of BTX (RT (benzene) = 2.9 min, RT (toluene) = 3.5 min, RT (m-xylene) = 4.5 min, RT (p-xylene) = 4.6 min and RT (o-xylene) = 5.1 min)

3. Results and discussion

No specific time evolution is noted for the concentrations of the carbonyl and aromatic compounds, as depicted for instance for formaldehyde on Figure 3. The only exception is for m,p-xylenes, with values between 3 and 16 µg.m^{-3} until December 2013, and between 1 and 5 µg.m^{-3} after this period. At the same time, the concentrations of o-xylene show a slightly larger dispersion after December 2013 than before. No reason has been found for this effect. Therefore, in the following analysis, the results from the different sampling dates will be lumped by site

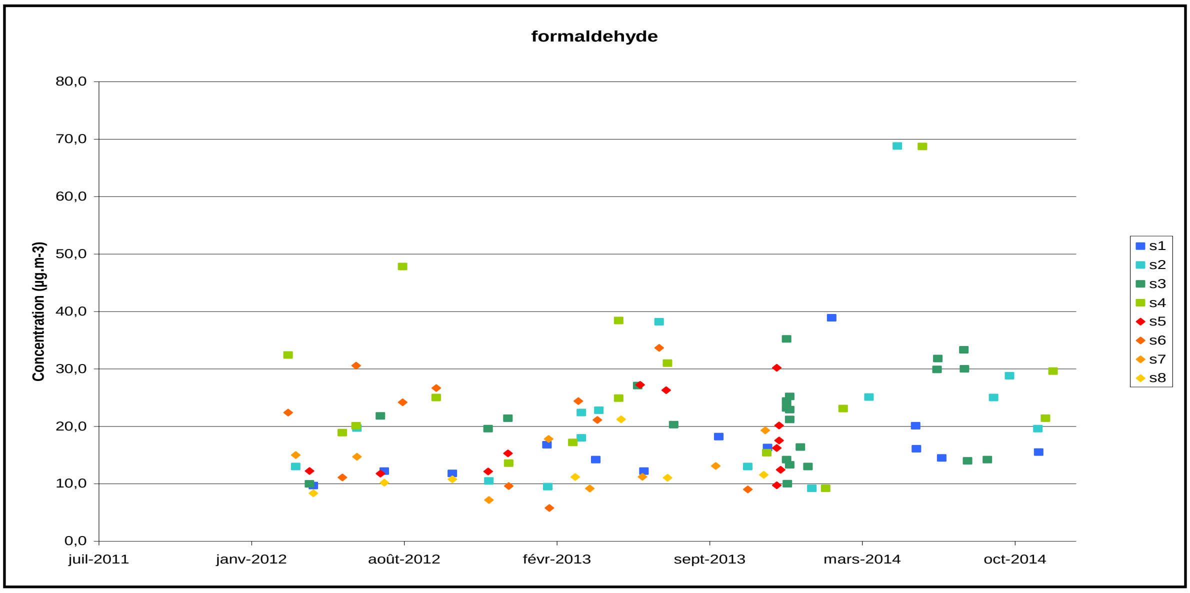

Figure 3: Evolution of formaldehyde at the sampling sites.

3.1. Mean concentrations values of BTX and carbonyls

Table 2 and Table 3 summarize respectively the concentrations of carbonyl compounds and BTX measured at the sampling sites of Inezgane and Ait Melloul. For each site, at least 10 samples were collected over the three years of the study (2012-2014). BTX concentrations are much more homogeneous, with toluene being the most abundant pollutants, with average concentrations ranging between 9 and 13 µg.m^{-3}, depending on the site considered. The maximal concentrations, above 20 µg.m^{-3}, are observed in Inezgane, while concentrations at Ait Melloul reach only 15 µg.m^{-3}. Average concentrations of benzene range from 2.6 to 6.5 µg.m^{-3}, with slightly higher concentrations observed in Inezgane. In the same way, o-xylene concentrations are also higher in Inezgane, with average values of 4-5 µg.m^{-3} whereas they are only around 2-3 µg.m^{-3} in Ait Melloul. Only m,p-xylenes show a different behavior, and their average concentration is higher in Ait Melloul (6-8 µg.m^{-3}) than in Inezgane (4-7 µg.m^{-3}). However, measurements of BTX in Ait Melloul were performed only in 2013, when a possible contamination of the cartridges may have occurred, as stated before.

Table 2: Average concentrations (µg.m^{-3}) for formaldehyde, acetaldehyde, acetone and benzaldehyde measured in Inezgane and Ait Melloul

Site	Benzene			Toluene			m,p-xylenes			o-xylene		
	Min	Max	Mean ± SD	Min	Max	Mean ± SD	Min	Max	Mean ± SD	Min	Max	Mean ± SD
Inezgane												
S1	0.7	11.0	5.5 ± 3.2	5.7	21.0	12.6 ± 4.9	1.3	13.8	5.6 ± 4.4	2.4	9.3	4.2 ± 2.2
S2	0.8	9.2	3.8 ± 3.4	5.9	20.3	10.4 ± 5.2	1.1	16.1	6.6 ± 5.1	2.2	13.1	5.3 ± 2.9
S3	2.9	14.8	6.5 ± 3.1	9.3	29.9	13.1 ± 4.9	1.0	14.8	3.6 ± 4.2	1.9	11.4	4.5 ± 2.7
S4	2.4	9.5	5.5 ± 2.3	5.8	19.5	11.8 ± 4.1	1.1	16.2	7.1 ± 5.0	1.4	11.0	4.9 ± 3.1
Ait Melloul												
S5	2.2	7.5	4.4 ± 2.3	7.9	11.2	8.7 ± 1.2	1.2	10.2	6.2 ± 3.3	1.1	4.9	2.3 ± 1.4
S6	2.1	7.0	4.9 ± 2.1	7.9	10.0	8.9 ± 1.0	3.2	11.3	8.7 ± 3.2	1.2	4.2	2.5 ± 1.5
S7	2.2	3.2	2.6 ± 0.4	8.0	13.1	10.8 ± 2.0	3.5	11.8	8.2 ± 3.2	0.9	3.1	1.9 ± 0.8
S8	2.5	7.7	4.8 ± 2.4	8.4	14.7	10.4 ± 2.5	4.6	9.9	7.1 ± 2.0	1.4	4.3	2.5 ± 1.2

The average concentrations of all these compounds allow classifying the sampling sites. Sites S7 and S8 in Ait Melloul are the least polluted places investigated, with an average total carbonyl concentrations of 47.2 and 39.6 µg.m^{-3} respectively. Site S1 of Inezgane and site S5 of Ait Melloul present a total concentration of 56.4 and 54.9 µg.m^{-3} respectively. Sites S3 and S6 have a total concentration of about 65 µg.m^{-3}, and sites S2 and S4, both in Inezgane, present high carbonyl concentrations of 71.4 and 83.1 µg.m^{-3} respectively. For BTX compounds, there are only minor differences in the sum concentrations between the sites, from 21.6 µg.m^{-3} for site 5 in Ait Melloul to 29.2 µg.m^{-3} in site 2 of Inezgane. These results show that S2 and S4 are the most polluted sites in the Inezgane area. Indeed, they are the two spots with the most traffic in the city. Moreover, near S2 are located wood industry units that make a large use of organic solvents, such as chlorophenol, formaldehyde, cetones and xylenes. S4 concentrates most of the traffic, with a nationwide bus terminal, a local and long distance taxi station, and a commercial center drawing many private vehicles. In addition, it is surrounded by high buildings that block the wind and prevent the dispersion of pollutants. S3 is also a zone of high traffic, close to industrial units, but as it is surrounded by low buildings, it is a windy zone, and the dispersion of pollutants is more efficient, leading to lower concentrations of pollutants than in S2 and S4. S1 is also a major crossroads with heavy traffic, but far from industrial units, and close to a forest area, which explains the comparatively low pollutant concentrations reported here. In Ait Melloul, the highest pollution levels are found at S5 and S6, which are characterized by extremely slow and frequent congestion. In spite of being downwind of industrial units, the pollution pattern still corresponds mainly to traffic. Site S7, though located in an industrial zone, was less polluted, probably due to less traffic in this area than in the S5, S6 and S8 sampling sites. Finally, site S8, in a suburban, windy zone, shows the lowest VOC levels.

The carbonyl and BTX levels observed in the present study are comparable to the roadside levels measured in several areas in Morocco and other cities over the world, presented in Table 4 and Table 5.

The aldehyde levels measured in the present study are of the same order of magnitude than the other studies reported in Table 3, except for Anza city in Morocco [25], strongly influenced by industrial emissions, Mexico City [35], and the Brazilian cities of Rio de Janeiro [36] and Salvador [37, 38], where the use of oxygenated fuel leads to even higher concentration levels. Still, these levels are comparable to the values measured in ambient air in cities in Taiwan [39], China [40] or India [18]. The BTX concentrations measured in the present study are two to ten times lower than the ones observed in other roadside environments, in large cities in Thailand, China, or Vietnam. As mentioned above, all the sampling sites are located close to the roads, so vehicular emissions are responsible for more than 80% of total VOC emission [49,50], and are therefore the main source of ambient VOC. The BTX and carbonyl levels measured here at any site would depend upon traffic flow, affected by temporary changes in activities and meteorology. The photochemical reactions and dispersion of pollutants affect strongly also their concentrations in the atmosphere.

Table 4 : Comparison between carbonyl levels ($\mu g\ m^{-3}$) in the roadside environment of Inezgane, Ait Melloul and of other cities.

Location	Formaldehyde		Acetaldehyde		Benzaldehyde		Acetone		References
	Range	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	
Inezgane-Ait Melloul, Morocco	5.8 - 68.8	18.9 ± 5.0	7.1- 48.0	17.8 ± 4.3	1.1 - 12.6	4.3 ± 1.3	5.1- 58	20.0 ± 4.7	This study
Anza, Morocco	17.5 - 178.1	60.5 ± 29	17.1-122.3	44.2 ± 22	3.1 - 16.6	7.2 ± 2.2	-	-	[25]
Kwai Chung, Hong Kong	-	16.7	-	13,9	-	-	-	-	[41]
Rio de Janeiro, Brazil	-	18.3 ± 21.1	-	26.3 ± 25.6	-	-	-	-	[36]
Bangkok, Thailand	5.1-17,2	11.5	1.6-7.95	3.5	-	-	-	-	[42]
Lapa bus station, Salvador, Brazil	81.2 -113	97.9 ± 19.7	126.5-169.5	148.1 ± 25.2	7.9 - 21.7	13.9 ± 2.2	-	-	[37]
Salvador, Brazil	-	54.0	-	124.3	-	-	-	-	[38]
Salvador, Brazil	-	23	-	10	-	-	-	-	[43]
Mexico city, Mexico (urban sites)	-	43.5	-	28.6	-	-	-	-	[35]
Nan-Chie site- Kaohsiung city. Taiwan (ambient air)	9.5 - 35.9	18.3 ± 7.2	8.4 - 24.3	14.9 ± 3.9	0.4 - 3.5	1.6 ± 0.6	-	1.23 ± 0.2	[39]
Hsiung - Kong site Kaohsiung city. Taiwan (ambient air)	7.3 - 39.4	18.7 ± 8.1	7.2 - 26.9	15.7 ± 4.3	0.4 - 4.5	2.2 ± 0.9	-	-	[39]
Beijing, China (ambient air)	-	14.8	-	10.2	-		-	16.6	[13]
Rome, Italy (ambient air)	-	22.8	-	18.3	-		-	17.6	[44]

Table 5: Comparison between BTX levels (µg. m^{-3}) in the roadside environment of Inezgane Ait Melloul and of other cities

Location	Benzene		Toluene		m.p-o-Xylene		References
	Range	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	
Inezgane- Ait Melloul city	0.7 - 14.8	4.8 ± 1.2	5.7 - 29.9	10.8 ± 1.6	1.2 - 14.6	10.1 ± 2.9	This study
Anza locality	3.6 - 27.2	12.9 ± 3.5	13.9 - 78.9	36.9 ± 6.5	4.4 - 29.6	16.2 ± 2.6	[27]
Bangkok, Thailand	1.2 - 29	11 ± 4.6	9.8 – 91	33 ±12	2.8 – 35	12 ± 4.8	[22]
	0.5 - 29	9.7 ± 4.5	1.5 – 91	30 ± 13	2.1-35	11 ± 4.7	
Nanjing, China	-	6.4 ± 3.8	-	19.8 ± 10.3	-	5.5 ± 4.1	[45]
Hong Kong, China	-	26.7 ± 33.0	-	77.2 ± 74.4	-	-	[46]
East Asia, Vietnam	23-39	32 ± 5	39-84	58 ± 14	-	-	[23]
Ho Chi Minh City, Vietnam	6-53	22	18-170	-	-	-	[47]
Ho Chi Minh City, Vietnam	-	56	-	121	-	-	[48]

During daytime, the main sink reactions for formaldehyde are the photolysis and the attack by the OH radical, with a rate constant k (OH+CH_2O) of 8.46×10^{-12} cm^3.molecule^{-1}.s^{-1} at room temperature [51]. Considering an average OH concentration of ~1×10^6 molecule.cm^{-3}, the formaldehyde atmospheric lifetime is 1.4 days. Generally, the average concentration of formaldehyde is higher than the concentrations of acetaldehyde and of benzaldehyde. However sometimes formaldehyde level was found in this work to be lower than acetaldehyde level. Certainly, acetaldehyde is the second most emitted gas from diesel fuel [52], but in the absence of any specific source of acetaldehyde in the Inezgane Ait Melloul area, no explanation can be found for this anomaly, except a possible contamination during the preparation of these few cartridges where H_2CO level is found to be lower than CH_3CHO level. The formaldehyde/acetaldehyde ratio obtained in the present study is on average around 1, with individual values in the range 0.3-3.0. This ratio values agree with the widely reported values in other areas [13-53], largely below the value of 10 typical of vegetation areas where the photo-oxidation of natural hydrocarbons such as isoprene yields more formaldehyde than acetaldehyde [54, 55]. Benzene and toluene react very slowly with O_3 (k <10^{-20} cm^3.molecule^{-1}.s^{-1}) [56] and NO_3 radicals, with a rate constant of 3×10^{-17} cm^3.molecule^{-1}.s^{-1} for benzene and 6.8×10^{-17} cm^3 .molecule^{-1}.s^{-1} for toluene [57]. Their atmospheric depletion is only via their reaction with OH radicals, with rate constants of 1.2×10^{-12} cm^3.molecule^{-}1.s^{-1} [58] and 5.9×10^{-12} cm^3.molecule^{-}1.s^{-1} [59] respectively. Assuming the common steady state concentration of OH radicals in the atmosphere of 1×10^6 molecule.cm^{-3}, the atmospheric lifetimes for benzene and toluene are 8.3 and 2.1 days respectively [60]. These two species are relatively stable compounds that can remain in the atmosphere for a long time. The rate constants for the reaction of xylenes with OH are 2.14×10^{-11} cm^3.molecule^{-1}.s^{-1} for m-xylene and 1.2×10^{-11} cm^3.molecule^{-}1.s^{-1} for o- and p-xylene [61]. Their atmospheric lifetime is only of 0.5 to 0.8 days [60] and consequently they will degrade more rapidly than benzene and toluene.

3.2. Qualitative influence of photochemistry on carbonyl levels

Aldehydes are both primary and secondary pollutants [62]. Their high concentrations during the morning imply the important contribution of primary sources. Aldehydes levels in ambient atmosphere result from the competition between their photochemical formation in situ as oxidation products of anthropogenic VOC compounds and their fast loss by photolysis and by reaction with OH radicals. Grosjean and Grosjean [63] showed that there is a net production of lower carbonyls (formaldehyde and acetaldehyde) on sunny days because of VOC reactions. The photodegradation of aldehydes is a significant source of OH radicals, which in turn accelerates the photo-oxidation of hydrocarbons present in air and further contributes to the formation of carbonyls. The fraction of formaldehyde produced photochemically can be estimated on the base of its concentration ratio to toluene, assuming that this later species comes exclusively from vehicle exhaust [17], which seems reasonable since our measurements did not point to specific toluene sources.

$$[\mathrm{HC(O)H}]_{Tot} = [\mathrm{HC(O)H}]_{exhaust} + [\mathrm{HC(O)H}]_{photochem} \qquad (2)$$

However, this method requires the knowledge of the aldehyde/toluene molar ratio in the vehicles exhaust fumes. These data are not available for the Moroccan vehicle fleet.

An alternative approach has been proposed by Satsumabayashi et al., [64] and Zhang et al.,[6], where the fraction of aldehyde produced by photochemical reactions $x_{\mathrm{photochem}}$ can be expressed as:

$$X_{\mathrm{photochem}} = \frac{\left(\frac{[\mathrm{RC(O)H}]}{[\mathrm{C_7H_8}]}\right)_{\mathrm{DT}} - \left(\frac{[\mathrm{RC(O)H}]}{[\mathrm{C_7H_8}]}\right)_{\mathrm{Lw}}}{\left(\frac{[\mathrm{RC(O)H}]}{[\mathrm{C_7H_8}]}\right)_{\mathrm{DT}}} \qquad (3)$$

where [RC(O)H] and [C_7H_8] are the concentrations of aldehyde and toluene, averaged over a period of 1 to 3 hours, DT and Lw correspond respectively to the average value during daytime and the lowest value of the day.
This approach was applied to formaldehyde. Samples were collected at the most polluted site, S4, with a 90-minute sampling duration, during four time intervals: 9:30-11:00, 12:00-13:30, 14:00-15:30 and 16:00-17:30. Measurements were repeated on four days in winter (December 2013 – February 2014) and four days in summer (Jun 2014 – August 2014).

Table 6: Evaluation of photochemical contribution in Inezgane (site S4).

	Winter period wind speed : 2.4 - 2.6 m/s HR% : 50.7 - 55.4% rain : 0.5 to 2.5 mm/3hr temperature °C : 13 – 15			Summer period wind speed : 1.8 - 2.8 m/s HR% : 21 - 35% rain : 0.4 to 2.5 mm/3hr temperature °C : 23 – 29		
Time	formaldehyde (µg/m^3)	toluene (µg/m^3)	FA/T	formaldehyde (µg/m^3)	toluene (µg/m^3)	FA/T
9:30-11:00	11.1 ± 1.0	9.4 ± 1.5	1.2	20.3 ± 1.8	12.7 ± 2.0	1.6
12:00-13:30	15.1 ± 2.2	11.5 ± 0.3	1.3	27.2 ± 7.3	10.8 ± 1.0	2.5
14:00-15:30	22.0 ± 3.1	11.3 ± 2.0	2.0	33.7 ± 4.2	11.1 ± 1.0	3.1
16:00-17:30	16.1 ± 1.5	12.1 ± 0.5	1.3	27.9 ± 6.8	10.4 ± 1.0	2.7

Table 6 presents the measured formaldehyde and toluene concentrations (average and standard deviation calculated from the individual values of the four days of measurements), together with the weather conditions. The low wind speed, especially in summer, limits the dispersion and therefore induces an accumulation of pollutants in the zone. The concentrations of aldehydes increase in the daytime due to photochemical reactions, followed by a decrease in the early evening as the produced aldehydes further react photochemically and decompose. A seasonal variation is noted, with concentrations higher in summer, by a factor ~2, indicating an increased contribution of the photochemistry in the generation of ambient carbonyls, related to higher temperatures and humidity [24]. Regarding toluene, no significant evolution during the day, or between the winter and summer periods, was observed.
From these measurements, we derive a contribution of photochemistry to the production of formaldehyde of ~20 % in winter, and of ~40 % in summer. This photochemical production of formaldehyde in Morocco is lower than the values of 53 % in Tokyo in summertime [64], of 30-35 % in wintertime and 80-90 % in summertime in Rome [17], and of 47.6 % in Beijing in summertime [6]. The relatively lower net production is probably due to the important photodecomposition under local atmospheric conditions.

Conclusion

The concentrations of carbonyls (formaldehyde, acetaldehyde, acetone and benzaldehyde) and BTX (benzene, toluene and xylenes) were measured for the first time in the roadside environment of the Inezgane-Ait Melloul area, Morocco, between 2013 and 2015, using active sampling onto 2,4-DNPH cartridges, subsequently analyzed by HPLC-UV, and onto SKC charcoal tubes, analyzed by GC-FID. The highest concentrations of carbonyls were found for acetone (20.0 ± 4.7 µg.m^{-3}), followed by formaldehyde (18.9 ± 5 µg.m^{-3}), acetaldehyde (17.8 ± 4.3) and benzaldehyde (4.3 ± 1.3 µg.m^{-3}). For BTX species analyzed, toluene was the most abundant aromatic compounds (10.8 ± 1.6 µg.m^{-3}), followed by xylenes (10.0 ± 2.9 µg.m^{-3}) and benzene (4.8 ± 1.2 µg.m^{-3}). These values correspond to the proximity, traffic-induced, pollution and not to background levels since all samplings were performed at roadside sites. The average concentrations of formaldehyde and acetaldehyde in Inezgane-Ait Melloul areas are well within the ranges reported in roadside environments of other urban cities. However, Anza locality in Morocco, Algiers in Algeria, Cairo in Egypt, Delhi and Kolkata in India, had much higher concentration levels of BTX or carbonyls than in Inezgane Ait Melloul roadside environment, due to industrial units, very high traffic or frequently congestion phenomena.

The contribution of photochemistry to the production of aldehydes was evaluated. The obtained values, of ~20 % in winter and ~40 % in summer, are lower than the ones obtained in other, large, cities over the world (Tokyo, Rome and Beijing), probably because of local meteorological conditions, and because the measurements were performed on freshly emitted air masses, which did not have had the time to manifest their photochemical potential.

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